Determination of Inorganic Salt Solubility by Headspace Gas Chromatography

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Abstract

Solubility of salts in aqueous solutions is an important parameter in many chemical engineering applications and industrial processes. Using conventional methods, it is very difficult to measure the solubility of salt in solutions with a complicated matrix, high viscosity, or at elevated temperatures. In this paper, we present a novel technique for solubility measurement using headspace gas chromatography (GC). It is based on the salting-out effect for the vapor-liquid equilibrium (VLE) of volatile organic compounds in aqueous solution [1-2]. For a set of salt solutions containing a volatile tracer, the headspace tracer concentration (measured by GC) at the VLE increases with the salt concentration in the solution until the solute reaches saturation. Thus, a transition point in the tracer concentration can be detected that corresponds to the salt solubility [3].

The aim of the present work was to explore headspace GC techniques that could be used for solubility measurements at temperatures above 100°C and to demonstrate a novel headspace technique that can simulate an industrial solvent evaporation process.

Method Development

1. Spiking headspace gas chromatographic method.

In this work, we observed that benzene alcohol (B-EthOH) is a better volatile tracer species than methanol, used in previous work [3], since its VLE behavior is also affected by salt concentration and provides a more distinct transition point at elevated temperature, as shown in Fig. 1.

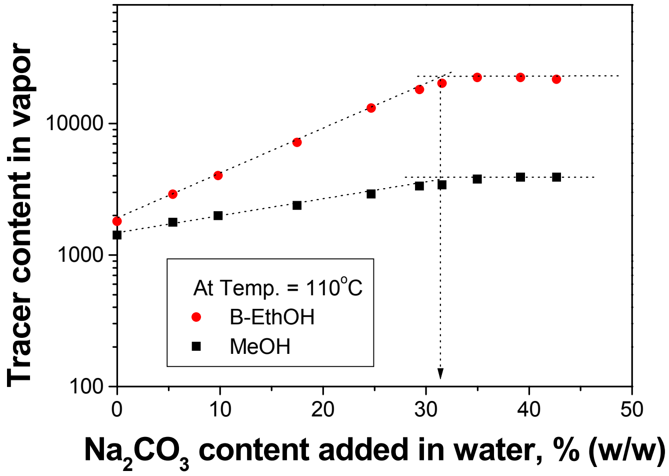

Fig. 1 An addition (spike) headspace GC measurement using indicated tracers to determine the solubility of sodium carbonate solution at 110°C.

Methanol has a relatively low boiling point (68°C); thus, more methanol will be present in the vapor phase together with water vapor at a elevated temperature. Benzene alcohol (B-EthOH) has a very high boiling point (~200°C); therefore, its VLE behavior is only significantly affected by the concentration of the salt in the solution at the studied temperature. According to this method (Fig. 1), the solubility of sodium carbonate at 110°C is 31.5 wt. % of solution, which is close to the value of 30.8% reported by Shi [4].

2. Multiple headspace extraction (MHE) gas chromatographic method.

Evaporation is a process that is widely used for concentrating the non-volatile species in solution. The commercial headspace GC system used in this work (HP-7694 automatic headspace sampler and HP-6890 capillary gas chromatograph) can be programmed for stepwise multiple headspace extraction. If the operating temperature is above the solution boiling point, water in the sample can be removed during each headspace extraction, thus, the evaporation process can be simulated using a small sample volume.

(a) Single salt solution

When a volatile tracer species such as benzene alcohol is also included in the studied solution, a change in its VLE behavior during the evaporation process can also indicate when crystal formation (precipitation) takes place. Fig. 2a shows the vapor tracer content change in the closed headspace sample vial during MHE at a temperature of 110°C for one salt-free solution and two salt-containing (sodium sulfate and carbonate) solutions.

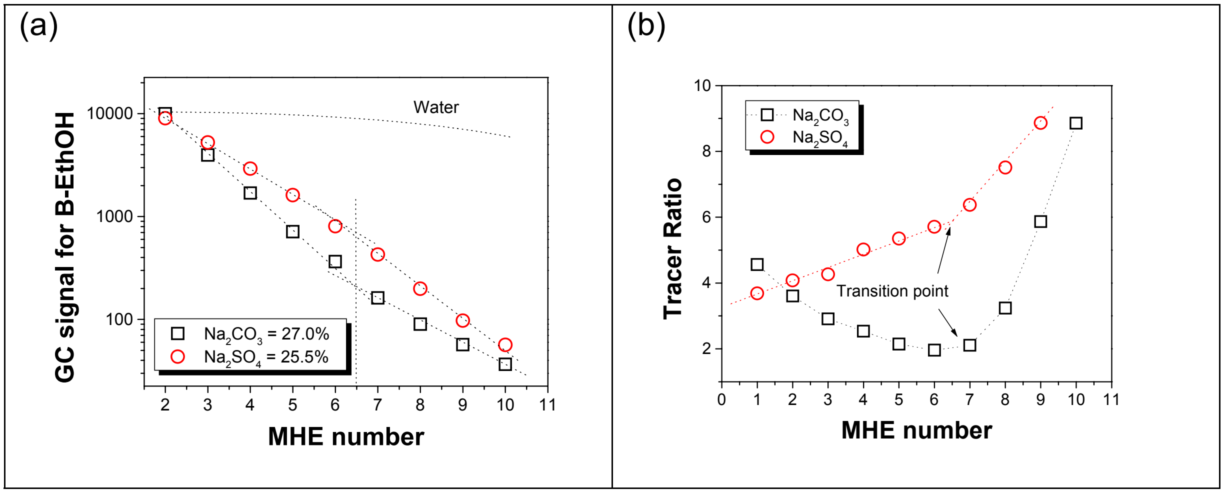

Fig. 2 (a). MHE measurement of the vapor tracer for sodium carbonate, sulphate salt and salt-free solutions. (b). Tracer ratio profiles for the single salt solutions during MHE process.

It was observed and mathematically proven that there is a linear relationship between the logarithm of the volatile species content in the vapor phase and the headspace extraction numbers in a partial headspace replacement system, in which the VLE of the volatile species is achieved [5-6]. This result implies that the vapor concentration decreases exponentially with the number of headspace extractions for unchanging liquid volume. Surprisingly, similar behavior was observed in the MHE (evaporation) process before crystal formation although the liquid volume is continually reduced. However, sodium carbonate and sodium sulfate solutions showed different behavior after precipitation occurred; specifically, the vapor tracer concentration in the sodium sulfate saturated solution decreased more rapidly than for the sodium carbonate solution.

Compared with the salt-free solution, the benzene alcohol tracer content in the vapor dramatically decreases for the salt-containing solutions due to the salting-out effect. The transition points were observed in the salt-containing solutions, because the VLE behavior during solvent removal is distinctly different than during the precipitation. Thus, the salt solubility can be calculated if 1) the salt concentration in the starting solution and 2) the amounts of water loss at the transition points are known. It was noticed that even slightly scattered data may lead to difficulty in determining the transition point. Therefore, we also evaluated a tracer ratio method for determination of the transition point as shown in Fig 2b. In this method, two tracers (benzene alcohol and methanol) were added to the studied solutions and HSGC was used to measure their vapor contents. The tracer ratio (R_i) can be calculated based on the GC headspace measurement signals (A) at the i^{th} headspace extraction, i.e.,

$$R_i = \frac{A_{B-EthOH,i}}{A_{MeOH,i}}$$

Tracking the ratio, a relative value, can minimize the uncertainty of using a single tracer. A more distinct transition can be observed using the tracer ratio method (Fig. 2b).

It should be pointed out that the ratio profiles can change if the relative concentrations of the two tracers added in tested solutions are different; however, the transition point corresponding to salt precipitation will be the same regardless of the relative initial concentrations of the two tracers.

The amount of water removal can be determined by conducting a repeat sample test under identical experimental conditions except for the number of headspace extractions. The number of extractions for the repeat test is the MHE number at the transition point observed in the previous test. By weighing the total sample vial before and after the second test at the transition extraction number, the water loss at the transition point can be determined by difference. The solubilities of sodium sulfate and sodium carbonate at 110 °C by the MHE experiments shown in Fig. 2 are 30.6 and 31.9 wt %, respectively, which matches with data from the literature [4].

(b) Bi-salt solutions

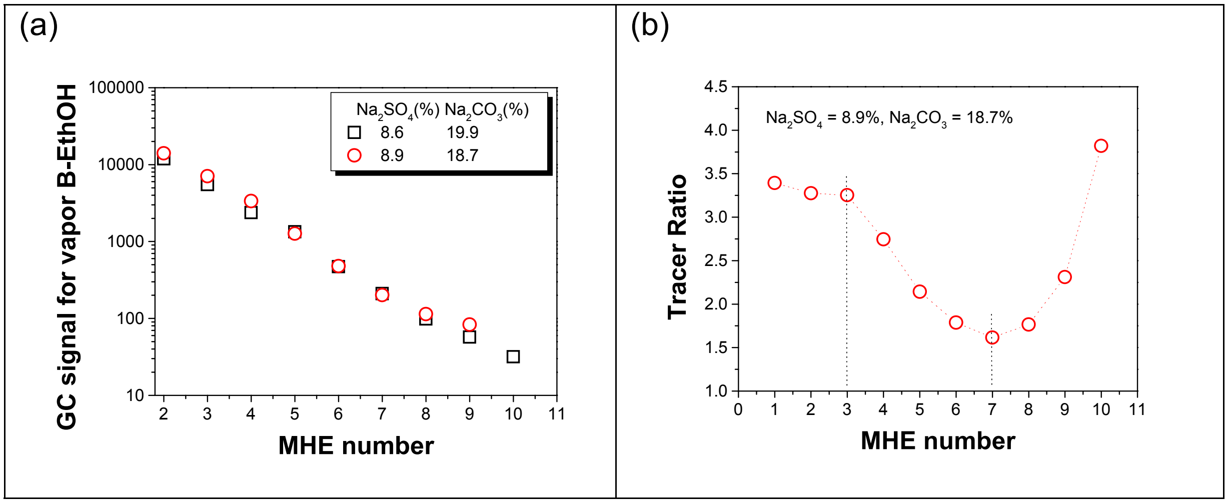

Fig. 3 (a).MHE GC measurement of a bi-salt solution (carbonate-sulfate molar ratio ~3:1). (b). Tracer ratio profile for a bi-salt solution during MHE process.

We also conducted MHE GC measurements for a sodium carbonate-sulfate salt mixture with an initial molar ratio of 3:1 at a temperature of 110°C (Fig. 3a). Similar to results in the single-salt solutions, the tracer ratio method provides a more distinct transition point during MHE measurements for the bi-salt solution as shown in Fig. 3b. There are two transition points indicated at MHE numbers 3 and 7, which correspond to crystallization points at 30.8 and 36.0 wt %, respectively. For an initial liquid composition with a Na_2CO_3/Na_2SO_4 molar ratio of 3:1, burkeite ($Na_2CO_3 \cdot 2Na_2SO_4$) is expected to be the first crystal formed in the MHE process (extraction number 3). According to Shi's work [4], a carbonate-rich species ($\sim 2Na_2CO_3 \cdot Na_2SO_4$) will be formed after burkeite precipitation upon further solvent removal. However, trace amounts of Ca^{2+} can inhibit the nucleation of both burkeite and dicarbonate [4, 7] creating a complex series of crystallization events during solvent removal of impure Na_2CO_3-Na_2SO_4 solutions. Our on-going work suggests that thermonatrite ($Na_2CO_3 \cdot H_2O$) is co-precipitated with dicarbonate in the presence of Ca^{2+}. There were trace amounts of Ca^{2+} in the salt mixture used for the MHE GC measurements in Fig. 3. We currently believe that precipitation of the hydrated $Na_2CO_3 \cdot H_2O$ salt is responsible for the second transition point observed in Fig. 3b.

(c) Kraft process black liquor

Pulp and paper industry kraft process black liquor samples were tested by the present method at a temperature of 110°C and the MHE GC measurement results are shown in Fig. 4. A small amount of benzene alcohol was added to warmed black liquor and mixed well before testing. There are two transition points during the MHE process (a.k.a., simulated black liquor evaporation) in both tested black liquor samples. In sample BL-1, the starting total solid content was 45.1 wt.% with 6 wt.% Na_2CO_3 (dry solids basis). In sample BL-2, the starting total solid content was 46.2 wt.% with 10 wt.% Na_2CO_3 (dry solids basis); the latter was made up by spiking sodium carbonate into BL-1. The solids contents at the two transition points for BL-1 are 57.8 and 61.1 %, respectively, and the solids contents at the two transition points for BL-2 are 57.2 and 59.7 %, respectively.

Dissolved lignin is a major component of the total solid content in black liquor. Our previous study [8] showed that the dissolved lignin effect on methanol Henry's law constant is not significant. Later, we found that salting-out effect of one-valence anions (typically hydroxide, hydrosulfide, and chloride in black liquor) on methanol Henry's law constant is less significant than that of two-valence anions (typically carbonate and sulfate) [3]. Therefore, the vapor tracer removal because of the salting effect caused by the two valence anions, mainly carbonate and sulfate in black liquor, during the MHE process is much slower than that found in the pure signal salt and bi-salt solutions. For example, the sodium carbonate content is 2.7 % in 45.1 % black liquor (BL-1), and it only increases to 3.5 % at the first transition point. With such a small change in salt content, it makes a more distinct transition point in MHE measurements when a signal tracer, benzene alcohol -- a non-process species in wood pulping, was applied.

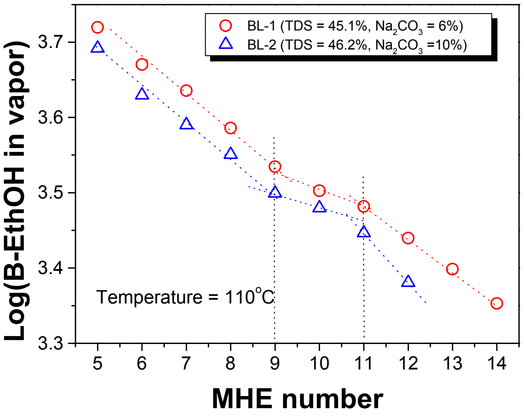

Fig. 4 MHE GC measurement on black liquor samples.

Although it remains to be verified experimentally, the two transition points are expected to correspond to the sequential precipitation of burkeite and dicarbonate salts. In a similar manner to the results shown in Fig. 4, addition of sodium carbonate to black liquor has been shown to decrease the solids content for the onset of crystallization of both burkeite and dicarbonate [9].

Conclusion

Two rapid headspace gas chromatographic techniques were demonstrated for the determination of salt solubility in water and a complex industrial matrix solution at industrially-significant temperatures. These methods eliminate the problems of accurate solubility determinations, which are typical of conventional sample filtration and composition analysis techniques. The headspace GC techniques can easily be automated to allow for rapid determination of solubility in a large experimental matrix.

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